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The attached documents are exact copies of the European patent application conformes à la version page, as originally filed.

Les documents fixés à cette attestation sont initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet nº

99810901.1

# PRIORITY **DOCUMENT**

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

> Der Präsident des Europäischen Patentamts; Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets p.o.

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## Blatt 2 der Bescheinigung Sheet 2 of the certificate Page 2 de l'attestation

Anmeldung Nr.: Application nc.: Demande n\*:

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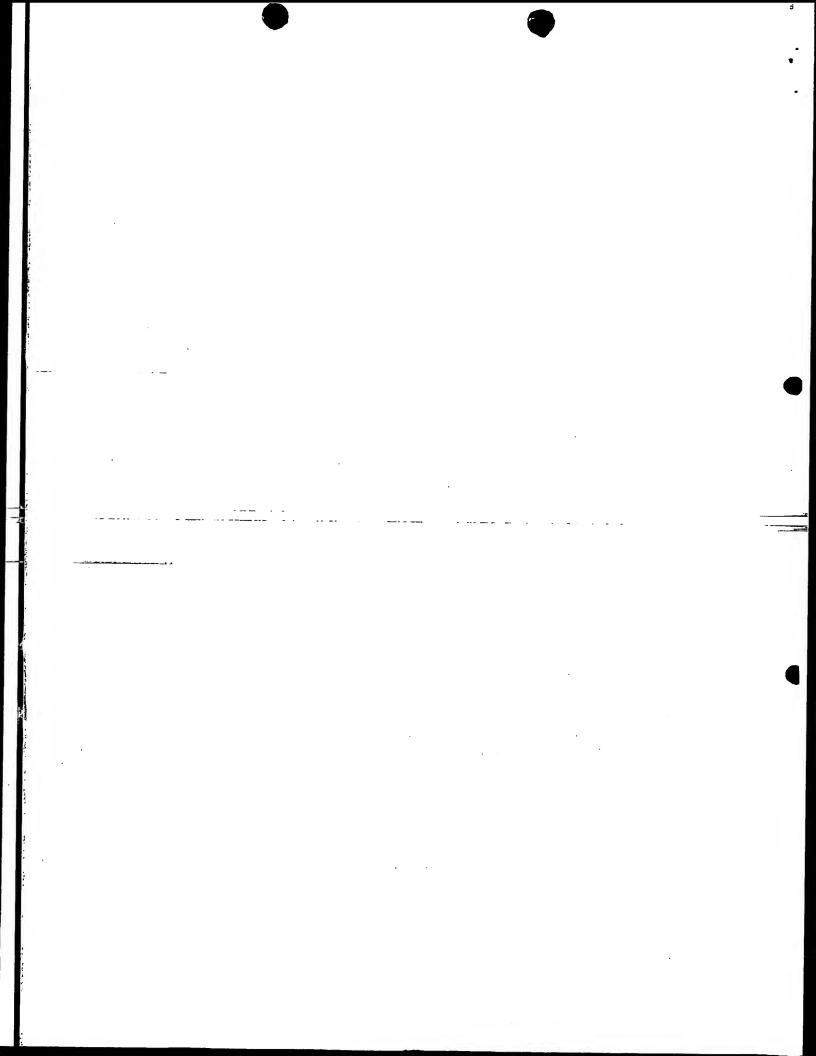
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See for original title of the application page 1 of the description

Remarques:



## Improved fabric softener compositions

#### FIELD OF THE INVENTION

The present invention relates to the use of selected polyorganosiloxanes, or mixtures thereof, liquid rinse conditioner compositions or tumble dryer sheet compositions and to the rinse-added and tumble dryer sheet compositions themselves. In particular it relates to textile softening compositions for use in a textile laundering operation to provide liquid rinse conditioners or tumble dryer sheets which impart excellent antipilling benefits on the textile.

## BACKGROUND OF THE INVENTION

As is well known, the pill formed on worn clothing markedly detracts from the appearance and feel of the clothing. The occurrence of pill is particularly a problem in the field of knitted materials, so that it has been greatly desired to seek measures for preventing the occurrence of pill on knitted fibre materials. Methods of improving the feel of worn clothing are known, such as rinse-added softener compositions. Typically, such compositions contain a water-insoluble quaternary-ammonium fabric softening agent. Silicones have also been used in rinse-cycle softening compositions for various reasons.

Surprisingly, it has been found that the use of selected polyorganosiloxanes, or mixtures thereof, in liquid rinse conditioner compositions provide excellent antipilling effects when applied to fabrics during a textile laundry operation.

Similar benefits are noted when compositions of the current invention are incorporated into tumble dryer additives such as impregnates on sheets.

A further object of the invention is to provide such liquid rinse conditioner compositions and tumble dryer sheets which provide improved antipilling effects when applied to fabrics.

## SUMMARY OF THE INVENTION

This invention relates to the use of compositions which comprise: dispersed polyorganosiloxanes of formula (1)

-2-

(1) 
$$R^{1} - S_{1} - O = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ CH_{3} \end{bmatrix} = \begin{bmatrix} CH_{$$

#### wherein

R<sup>1</sup> is OH, OR<sup>2</sup> or CH<sub>3</sub>
R<sup>2</sup> is CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>
R<sup>3</sup> is CH<sub>3</sub>, CH<sub>2</sub>CHR<sup>4</sup>CH<sub>2</sub>NHR<sup>5</sup>, or CH<sub>2</sub>CHR<sup>4</sup>CH<sub>2</sub>N(COCH<sub>3</sub>)R<sup>5</sup>

or (4) 
$$(CH_2)_3$$
  $NR^8$ 

 $R^4$  is H or  $CH_3$   $R^5$  is H,  $CH_2CH_2NHR^6$ ,  $C(=O)-R^7$  or  $(CH_2)_Z$ - $CH_3$ z is 0 to 7  $R^6$  is H or  $C(=O)-R^7$   $R^7$  is  $CH_3$ ,  $CH_2CH_3$  or  $CH_2CH_2CH_2OH$   $R^8$  is H or  $CH_3$ the sum of X and Y is 40 to 1500

or a dispersed polyorganosiloxane which comprises at least one unit of the formula (5);

(5) 
$$(R^9)_V (R^{10})_W \text{Si-A-B}$$

wherein

 $R^9$  is  $CH_3$ ,  $CH_3CH_2$  or Phenyl  $R^{10}$  is -O-Si or -O- $R^9$  the sum of v and w equals 3, and v does not equal 3  $A = -CH_2CH(R^{11})(CH_2)_K$ 

 $B = -NR^{12}((CH_2)_1-NH)_mR^{12}$ , or

n is 0 or 1 when n is 0,  $U^1$  is N, when n is 1,  $U^1$  is CH I is 2 to 8 k is 0 to 6 m is 0 to 3  $R^{11}$  is H or CH<sub>3</sub>  $R^{12}$  is H, C(=O)- $R^{16}$ , CH<sub>2</sub>(CH<sub>2</sub>)<sub>p</sub>CH<sub>3</sub> or

p is 0 to 6
R<sup>13</sup> is NH, O, OCH<sub>2</sub>CH(OH)CH<sub>2</sub>N(Butyl), OOCN(Butyl)
R<sup>14</sup> is H, linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl, Phenyl or CH<sub>2</sub>CH(OH)CH<sub>3</sub>

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R<sup>15</sup> is H or linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl R<sup>16</sup> is CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub> or (CH<sub>2</sub>)<sub>q</sub>OH q is 1 to 6 U<sup>2</sup> is N or CH.

or a dispersed polyorganosiloxane of the formula (8);

(8) 
$$R^{17} - S_{i} - O = CH_{3} - CH_$$

#### wherein

R3 is as previously defined

R<sup>17</sup> is OH, OR<sup>18</sup> or CH<sub>3</sub>

R<sup>18</sup> is CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>

 $R^{19}$  is  $R^{20}$ -(EO)<sub>m</sub>-(PO)<sub>n</sub>- $R^{21}$ 

m is 3 to 25

n is 0 to 10

R<sup>20</sup> is CH<sub>2</sub>CH(R<sup>22</sup>)(CH<sub>2</sub>)<sub>p</sub>R<sup>23</sup>

p is 1 to 4

 $R^{21}$  is H,  $R^{24}$ ,  $CH_2CH(R^{22})NH_2$  or  $CH(R^{22})CH_2NH_2$ 

R<sup>22</sup> is H or CH<sub>3</sub>

R<sup>23</sup> is O or NH

R<sup>24</sup> is linear or branched C<sub>1</sub>-C<sub>8</sub> alkyl or Si(R<sup>25</sup>)<sub>3</sub>

R<sup>25</sup> is R<sup>24</sup>, OCH<sub>3</sub> or OCH<sub>2</sub>CH<sub>3</sub>

EO is -CH2CH2O-

PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O-

the sum of X1,Y1 and S is 40 to 1500

or a dispersed polyorganosiloxane of the formula (9);

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R<sup>26</sup> is linear or branched C<sub>1</sub> - C<sub>20</sub> alkoxy, CH<sub>2</sub>CH(R<sup>4</sup>)R<sup>29</sup>

R4 is as previously defined

R<sup>29</sup> is linear or branched C<sub>1</sub> - C<sub>20</sub> alkyl

 $R^{27}$  is aryl, aryl substituted by linear or branched  $C_1$  -  $C_{10}$  alkyl, linear or branched  $C_1$  -  $C_{20}$  alkyl substituted by aryl or aryl substituted by linear or branched  $C_1$  -  $C_{10}$  alkyl  $R^{28}$  is

the sum of X<sup>2</sup>, X<sup>3</sup>, X<sup>4</sup> and Y<sup>2</sup> is 40 to 1500, wherein X<sup>3</sup>, X<sup>4</sup> and Y<sup>2</sup> may be independently of each-other-0;

The composition is preferably used as a component in a liquid rinse conditioner composition. The textile fibre materials are preferably treated for antipilling.

In tumble dryer applications the compositions are usually incorporated into impregnates on non-woven sheets. However, other application forms are known to those skilled in the art.

The liquid rinse conditioner will be used after the textile fibre materials have been washed with a laundry detergent, which may be one of a broad range of detergent types. The tumble dryer sheet will be used after a laundering process. The textile fibre materials may be damp or dry.

The dispersed polyorganosiloxane composition or the liquid rinse conditioner composition may also be sprayed directly onto the fabrics prior to or during the ironing or drying of the treated fabrics.

The polyorganosiloxane may be anionic, nonionic or cationic, preferably nonionic or cationic.

The polyorganosiloxanes, or mixtures thereof, are used in a dispersed form, via the use of an emulsifier. The polyorganosiloxane aqueous emulsion contains a water content of 25 to 90% by weight based on the total weight of the emulsion.

When the polyorganosiloxane contains a nitrogen atom, the nitrogen content of the aqueous emulsion due to the polyorganosiloxane is from 0.001 to 0.25 % with respect to the silicon content. The particles of the emulsion have a diameter of between 5nm and 1000nm.

The polyorganosiloxane aqueous emulsion has a solids content of 5 to 70% at a temperature of 120°C.

The polyorganosiloxane aqueous emulsion has a pH value from 2.5 to 9.0.

The aqueous polyorganosiloxane compositions may further comprise one or more components selected from dispersed polyethylene, dispersed fatty acid alkanol amide and polysilicic acid.

The aqueous polyorganosiloxane compositions may further comprise an additional polyorganosiloxane:

wherein g is

and G is C<sub>1</sub> to C<sub>20</sub> alkyl.

This polydimethylsiloxane is cationic, has a viscosity at 25°C of 250 mm<sup>2</sup>s<sup>-1</sup> to 450 mm<sup>2</sup>s<sup>-1</sup>, has a specific gravity of 1.00 to 1.02 g/cm<sup>3</sup> and has a surface tension of 28.5 mNm<sup>-1</sup> to 33.5 mNm<sup>-1</sup>.

The aqueous polyorganosiloxane compositions may further comprise an additional polyorganosiloxane, such as that known as Magnasoft HSSD, or a polyorganosiloxane of the formula:

R\_is\_CH2CH2CH2N(R\_)2

R<sup>™</sup> is linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl

R' is  $(CH_2)_{X'''}(EO)_{m}-(PO)_{n}-R''''$ 

m is 3 to 25

n is 0 to 10

X" is 0 to 4

R" is H or linear or branched C1-C4 alkyl

EO is -CH2CH2O-

PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O-

the sum of X', Y' and S' is 40 to 300.

Preferably the compositions comprise dispersed polyorganosiloxanes of formula (1):

-8-

(1) 
$$R^{i} - S_{i} - O = \begin{bmatrix} CH_{3} \\ | \\ | \\ CH_{3} \end{bmatrix} \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} \begin{bmatrix} CH_{3} \\ | \\ CH_{3} \end{bmatrix} \begin{bmatrix} CH_{3} \\ | \\ CH_{3} \end{bmatrix}$$

wherein

R1 is OH, OR2 or CH3

R2 is CH3 or CH2CH3

R<sup>3</sup> is CH₃, CH₂CHR⁴CH₂NHR⁵, or

R⁴ is H or CH₃

R<sup>5</sup> is H, CH<sub>2</sub>CH<sub>2</sub>NHR<sup>6</sup>, C(=O)-R<sup>7</sup>

 $R^6$  is H or C(=0)- $R^7$ 

R<sup>7</sup> is CH₃, CH₂CH₃ or CH₂CH₂CH₂OH

R<sup>6</sup> is H or CH<sub>3</sub>

the sum of X and Y is 40 to 1500

or a dispersed polyorganosiloxane which comprises at least one unit of the formula (5);

(5) 
$$(R^9)_V (R^{10})_W \text{Si-A-B}$$

wherein

R<sup>9</sup> is CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>

R<sup>10</sup> is -O-Si or -O-R<sup>9</sup>

the sum of v and w equals 3, and v does not equal 3

 $A = -CH_2CH(R^{11})(CH_2)_K$ 

B =

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$$R^{15}$$
  $R^{15}$   $CH_2$   $CH_2$   $CH_2$   $CH_2$   $CH_3$   $CH_4$   $CH_5$   $CH_$ 

n is 1

U<sup>1</sup> is CH

k is 0 to 6

R11 is H or CH3

R<sup>13</sup> is OOCN(Butyl)

R14 is H, linear C1-C4 alkyl, Phenyl

R15 is H or linear C1-C4 alkyl

U<sup>2</sup> is N

or a dispersed polyorganosiloxane of the formula (8);

wherein

R<sup>3</sup> is as previously defined

R<sup>17</sup> is OH, OR<sup>18</sup> or CH<sub>3</sub>

R18 is CH3 or CH2CH3

 $R^{19}$  is  $R^{20}$ -(EO)<sub>m</sub>-(PO)<sub>n</sub>- $R^{21}$ 

m is 3 to 25

n is 0 to 10

R<sup>20</sup> is CH<sub>2</sub>CH(R<sup>22</sup>)(CH<sub>2</sub>)<sub>p</sub>R<sup>23</sup>

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p is 1 to 4

R<sup>21</sup> is H, R<sup>24</sup>, CH<sub>2</sub>CH(R<sup>22</sup>)NH<sub>2</sub> or CH(R<sup>22</sup>)CH<sub>2</sub>NH<sub>2</sub>

R<sup>22</sup> is H or CH<sub>3</sub>

R<sup>23</sup> is O or NH

R<sup>24</sup> is linear or branched C<sub>1</sub>-C<sub>3</sub> alkyl or Si(R<sup>25</sup>)<sub>3</sub>

R<sup>25</sup> is R<sup>24</sup>, OCH<sub>3</sub> or OCH<sub>2</sub>CH<sub>3</sub>

EO is -CH<sub>2</sub>CH<sub>2</sub>O
PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O
the sum of X<sup>1</sup>, Y<sup>1</sup> and s is 40 to 1500

or a dispersed polyorganosiloxane of the formula (9);

$$(9) \quad H_{3}C - S_{i} - O = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{i} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S$$

 $R^{26}$  is linear  $C_1$  -  $C_{20}$  alkoxy,  $R^4$  is as previously defined  $R^{29}$  is linear  $C_1$  -  $C_{20}$  alkyl  $R^{27}$  is,  $CH_2CH(R^4)$ Phenyl  $R^{28}$  is

the sum of  $X^2$ ,  $X^3$ ,  $X^4$  and  $Y^2$  is 40 to 1500, wherein  $X^3$ ,  $X^4$  and  $Y^2$  may be independently of each other 0; or a mixture thereof.

Most preferred polyorganosiloxane aqueous emulsions comprise a polyorganosiloxane or mixture thereof of formula:

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(1) 
$$R^{1} - S_{1} - O = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ S_{1} - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ | \\ CH_{3} \end{bmatrix} = \begin{bmatrix} C$$

wherein R¹ is OH or CH₃, R³ is CH₃ or CH₂CHR⁴CH₂NHR⁵, R⁴ is H or CH₃, R⁵ is CH₂CH₂NHR⁶, R⁶ is H, and the ratio of X:Y is 25:1 to 220:1, preferably from 30:1 to 180:1. This polyorganosiloxane may be nonionic or cationic. When the siloxane contains nitrogen the nitrogen content of the aqueous emulsion due to this polyorganosiloxane is from 0.015 to 0.1%, preferably from 0.02 to 0.06 % with respect to the silicon content. This preferred polyorganosiloxane aqueous emulsion has a solids content of 15 to 50 %, preferably from 16 to 45 % at a temperature of 120°C. This preferred polyorganosiloxane aqueous emulsion has a water content of 50 to 83 % by weight based on the total weight of the emulsion. This preferred polyorganosiloxane aqueous emulsion has a pH in the range of 3.0 to 6.0. The polyorganosiloxane chain length, which is understood to be the sum of X and Y, is from 300 to 1500 siloxane units. These polyorganosiloxanes may be used in a composition which also comprises either a dispersed polyethylene or a fatty acid alkanol amide or a mixture of thereof.

Other most preferred polyorganosiloxane aqueous emulsions comprise a polyorganosiloxane or mixture thereof of formula (8):

(8) 
$$R^{17} - Si - O = \begin{bmatrix} CH_3 \\ I \\ Si - O \end{bmatrix} = \begin{bmatrix} CH_3$$

wherein  $R^{17}$  is OH or  $CH_3$ ,  $R^3$  is  $CH_3$ ,  $CH_2CHR^4CH_2NHR^5$ ,  $R^4$  is H or  $CH_3$ ,  $R^5$  is H,  $R^{19}$  is  $R^{20}$ - $(EO)_m$ - $(PO)_n$ - $R^{21}$  (where m is 3 to 25 and n is 0 to 10),  $R^{20}$  is  $CH_2CH(R^{22})(CH_2)_pR^{23}$  (where p is 1 to 4),  $R^{21}$  is H,  $R^{22}$  is H or  $CH_3$ ,  $R^{23}$  is O, EO is - $CH_2CH_2O$ -, PO is - $CH(CH_3)CH_2O$ - or - $CH_2CH(CH_3)O$ , the sum of  $X^1$ ,  $Y^1$  and S is 150 to 1500 and the ratio of X:S is 25:1 to 220:1, preferably from 30:1 to 180:1. This polyorganosiloxane may be nonionic or cationic. When the siloxane contains nitrogen the nitrogen content of the aqueous emulsion due to this

polyorganosiloxane is from 0.015 to 0.12 %, preferably from 0.02 to 0.08 % with respect to the silicon content. This preferred polyorganosiloxane aqueous emulsion has a solids content of 16 to 50 %, preferably from 18 to 45 % at a temperature of 120 °C. This preferred polyorganosiloxane aqueous emulsion has a water content of 50 to 82 % by weight based on the total weight of the emulsion. This preferred polyorganosiloxane aqueous emulsion has a pH in the range of 3.0 to 6.0. These polyorganosiloxanes may be used in a composition which also comprises a dispersed polyethylene. These preferred aqueous polyorganosiloxane compositions may further comprise an additional polyorganosiloxane:

wherein g is

and G is C<sub>1</sub> to C<sub>20</sub> alkyl. This polydimethylsiloxane is cationic, has a viscosity at 25°C of 250 mm<sup>2</sup>s<sup>-1</sup> to 450 mm<sup>2</sup>s<sup>-1</sup>, has a specific gravity of 1.00 to 1.02 g/cm<sup>3</sup> and has a surface tension of 28.5 mNm<sup>-1</sup> to 33.5 mNm<sup>-1</sup>.

Emulsifiers used to prepare the polyorganosiloxane compositions include:

- i) Ethoxylates, such as alkyl ethoxylates, amine ethoxylates or ethoxylated alkylammoniumhalides. Alkyl ethoxylates include alcohol ethoxylates or isotridecyl ethoxylates. Preferred alcohol ethoxylates include linear or branched nonionic alkyl ethoxylates containing 2 to 15 ethylene oxide units. Preferred isotridecyl ethoxylates include nonionic isotridecyl ethoxylates containing 5 to 25 ethylene oxide units. Preferred amine ethoxylates include nonionic C10 to C20 alkyl amino ethoxylates containing 4 to 10 ethylene oxide units. Preferred ethoxylated alkylammoniumhalides include nonionic or cationic ethoxylated C6 to C20 alkyl bis(hydroxyethyl)methylammonium chlorides.
- ii) Alkylammonium halides, preferably cationic quaternary ester alkylammonium halides.

- iii) Silicones, preferably nonionic polydimethylsiloxane polyoxyalkylene copolymers
- iv) Saccharides, preferably nonionic alkylpolyglycosides.

A mixture of these emulsifiers may also be used.

As mentioned previously, the aqueous polyorganosiloxane compositions may further comprise one or more components selected from dispersed polyethylene, dispersed fatty acid alkanol amide and polysilicic acid. These components are described below.

The emulsifiable polyethylene (polyethylene wax) is known and is described in detail in the prior art (compare, for example, DE-C-2,359,966, DE-A-2,824,716 and DE-A-1,925,993). The emulsifiable polyethylene is as a rule a polyethylene having functional groups, in particular COOH groups, some of which can be esterified. These functional groups are introduced by oxidation of the polyethylene. However, it is also possible to obtain the functionality by copolymerization of ethylene with, for example, acrylic acid. The emulsifiable polyethylenes have a density of at least 0.91 g/cm³ at 20°C., an acid number of at least 5 and a saponification number of at least 10. Emulsifiable polyethylenes which have a density of 0.95 to 1.05 g/cm³ at 20°C, an acid number of 10 to 60 and a saponification number of 15 to 80 are particularly preferred. This material is generally obtainable commercially in the form of flakes, lozenges and the like. A mixture of these emulsifiable polyethylenes may also be used.

The polyethylene wax is employed in the form of dispersions. Various emulsifiers are suitable for their preparation. The preparation of the dispersions is described in detail in the prior art.

Emulsifiers suitable for dispersing the polyethylene component include:

i) Ethoxylates, such as alkyl ethoxylates or amine ethoxylates. Alkyl ethoxylates include alcohol ethoxylates or isotridecyl ethoxylates. Preferred alcohol ethoxylates include nonionic fatty alcohol ethoxylates containing 2 to 55 ethylene oxide units. Preferred isotridecyl ethoxylates include nonionic isotridecyl ethoxylates containing 6 to 9 ethylene oxide units. Preferred amine ethoxylates include nonionic C10 to C20 alkyl amino ethoxylates containing 7 to 9 ethylene oxide units.

- ii) Alkylammonium halides, preferably cationic quaternary ester alkylammonium halides.
- iii) Ammonium salts, preferably cationic aliphatic quaternary ammonium chloride or sulfate.

A mixture of these emulsifiers may also be used.

Suitable fatty acid alkanolamides are for example monoalkanolamides or diakanolamides of the formulae:

R<sup>30</sup> being a saturated or unsaturated hydrocarbon radical containing 10 to 24 carbon atoms and c being a number from 1 to 10. Also suitable are alkanolamides that are derived from aromatic carboxylic acids, e.g. salicylic acid. If, as illustrated in the first-mentioned formula, two such alkanol radicals are bonded to the nitrogen atom, then c may obviously have a different value for one radical than for the other radical. A mixture of these fatty acid alkanolamides may also be used.

Emulsifiers suitable for dispersing the fatty acid amide component include:

- i) Ethoxylates, such as alkyl ethoxylates, amine ethoxylates or amide ethoxylates. Alkyl ethoxylates include alcohol ethoxylates or isotridecyl ethoxylates. Preferred alcohol ethoxylates include nonionic fatty alcohol ethoxylates containing 2 to 55 ethylene oxide units. Preferred isotridecyl ethoxylates include nonionic isotridecyl ethoxylates containing 5 to 45 ethylene oxide units. Preferred amine ethoxylates include nonionic C10 to C20 alkyl amino ethoxylates containing 4 to 25 ethylene oxide units. Preferred amide ethoxylates include cationic fatty acid amide ethoxylates containing 2 to 25 ethylene oxide units.
- ii) Alkylammonium halides, preferably cationic quaternary ester alkylammonium halides or cationic aliphatic acid alkylamidotrialkylammonium methosulfates.
- iii) Ammonium salts, preferably cationic aliphatic quaternary ammonium chloride or sulfate.

A mixture of these emulsifiers may also be used.

A composition containing a polyorganosiloxane dispersion used according to the present invention comprises:

- a) 2 to 70 % by weight based on the total weight of the composition of polyorganosiloxane, or a mixture thereof; preferably 2-to 35-%-by-weight-based on the total-weight-of-the composition of polyorganosiloxane, or a mixture thereof;
- b) 0.2 to 30 % by weight based on the total weight of the composition of an emulsifier, or a mixture thereof; preferably 0.2 to 10 % by weight based on the total weight the composition of an emulsifier, or a mixture thereof;
- c) 0 to 25 % by weight based on the total weight of the composition of a polyethylene, or a mixture thereof; preferably 0 to 12 % by weight based on the total weight of the composition of a polyethylene, or a mixture thereof;
- d) 0 to 20 % by weight based on the total weight the composition of a fatty acid alkanolamide, or a mixture thereof; preferably 0 to 8 % by weight based on the the composition of total weight of a fatty acid-alkanolamide, or a mixture thereof;
- e) 0 to 10 % by weight based on the total weight of the composition of a polysilicic acid; preferably 0 to 5 % by weight based on the total weight of the composition of a polysilicic acid;
- f) water to 100 %.

A further polyorganosiloxane dispersion used according to the present invention comprises:

- a) 2 to 70 % by weight based on the total weight of the composition of polyorganosiloxane, or a mixture thereof; preferably 2 to 35 % by weight based on the total weight of the composition of polyorganosiloxane, or a mixture thereof;
- b) 0.2 to 30 % by weight based on the total weight of the composition of an emulsifier, or a mixture thereof; preferably 0.2 to 10 % by weight based on the total weight the composition of an emulsifier, or a mixture thereof;
- c) 0 to 25 % by weight based on the total weight of the composition of a polyethylene, or a mixture thereof; preferably 0 to 12 % by weight based on the total weight of the composition of a polyethylene, or a mixture thereof;
- d) water to 100 %.

A further polyorganosiloxane dispersion used according to the present invention comprises:

- a) 2 to 70 % by weight based on the total weight of the composition of polyorganosiloxane, or a mixture thereof; preferably 2 to 35 % by weight based on the total weight of the composition of polyorganosiloxane, or a mixture thereof;
- b) 0.2 to 30 % by weight based on the total weight of the composition of an emulsifier, or a mixture thereof; preferably 0.2 to 10 % by weight based on the total weight the composition of an emulsifier, or a mixture thereof;
- c) 0 to 20 % by weight based on the total weight the composition of a fatty acid alkanolamide, or a mixture thereof; preferably 0 to 8 % by weight based on the the composition of total weight of a fatty acid alkanolamide, or a mixture thereof; d) water to 100 %.

The present emulsions can be prepared as follows: the polyorganosiloxane, polyethylene, fatty acid alkanol amide or polysilicic acid or mixtures thereof, are emulsified in water using one or more surfactants and shear forces, e.g. by means of a colloid mill. Suitable surfactants are described above. The components may be emulsified individually before being mixed together, or emulsified together after the components have been mixed. The surfactant(s) is/are used in customary amounts known to the person skilled in the art and can be added either to the polyorganosiloxane or to the water prior to emulsification. Where appropriate, the emulsification operation can, or in some cases, must be carried out at elevated temperature.

Another aspect of the present invention is a liquid rinse conditioner composition which comprises the dispersed polyorgansiloxane composition and a hydrocarbon based fabric softening component, such as conventional hydrocarbon based fabric softening components known in the art.

Hydrocarbon fabric softeners suitable for use herein are selected from the following classes of compounds:

(i) Cationic quaternary ammonium salts. The counter ion of such cationic quaternary ammonium salts may be a halide, such as chloride or bromide, methyl sulphate, or other ions well known in the literature. Preferably the counter ion is methyl sulfate or any alkyl

sulfate or any halide, methyl sulfate being most preferred for the dryer-added articles of the invention.

Examples of cationic quaternary ammonium salts include but are not limited to:

(1)-Acyclic quaternary-ammonium-salts-having-at-least-two-C<sub>8</sub>-to-C<sub>307</sub> preferably-C<sub>12</sub>-to-C<sub>22</sub> alkyl or alkenyl chains, such as: ditallowdimethyl ammonium methylsulfate, di(hydrogenated tallow)dimethyl ammonium methylsulfate, distearyldimethyl ammonium methylsulfate, dicocodimethyl ammonium methylsulfate and the like. It is especially preferred if the fabric softening compound is a water insoluble quaternary ammonium material which comprises a compound having two C<sub>12</sub> to C<sub>18</sub> alkyl or alkenyl groups connected to the molecule via at least one ester link. It is more preferred if the quaternary ammonium material has two ester links present. An especially preferred ester-linked quaternary ammonium material for use in the invention can be represented by the formula:

wherein each  $R^{31}$  group is independently selected from  $C_1$  to  $C_4$  alkyl, hydroxyalkyl or  $C_2$  to  $C_4$  alkenyl groups; T is either

and wherein each  $R^{32}$  group is independently selected from  $C_8$  to  $C_{28}$  alkyl or alkenyl groups; and e is an integer from 0 to 5.

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A second preferred type of quaternary ammonium material can be represented by the formula:

wherein R<sup>31</sup>, e and R<sup>32</sup> are as defined above.

- (2) Cyclic quaternary ammonium salts of the imidazolinium type such as di(hydrogenated tallow)dimethyl imidazolinium methylsulfate, 1-ethylene-bis(2-tallow-1-methyl) imidazolinium methylsulfate and the like;
- (3) Diamido quaternary-ammonium salts such as: methyl-bis(hydrogenated tallow amidoethyl)-2-hydroxethyl ammonium methyl sulfate, methyl bi(tallowamidoethyl)-2-hydroxypropyl ammonium methylsulfate and the like;
- (4) Biodegradable quaternary ammonium salts such as N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium methyl sulfate and N,N-di(tallowoyl-oxy-propyl)-N,N-dimethyl ammonium methyl sulfate. Biodegradable quaternary ammonium salts are described, for example, in U.S. Patents 4,137,180, 4,767,547 and 4,789,491 incorporated by reference herein.

Preferred biodegradable quaternary ammonium salts include the biodegradable cationic diester compounds as described in U.S. Patent 4,137,180, herein incorporated by reference.

(ii) Tertiary fatty amines having at least one and preferably two C8 to C30, preferably C12 to C22 alkyl chains. Examples include hardened tallow-di-methylamine and cyclic amines such as 1-(hydrogenated tallow)amidoethyl-2-(hydrogenated tallow) imidazoline. Cyclic amines which may be employed for the compositions herein are described in U.S. Patent 4,806,255 incorporated by reference herein.

- (iii) Carboxylic acids having 8 to 30 carbons atoms and one carboxylic group per molecule. The alkyl portion has 8 to 30, preferably 12 to 22 carbon atoms. The alkyl portion may be linear or branched, saturated or unsaturated, with linear saturated alkyl preferred. Stearic acid is a preferred fatty acid for use in the composition herein. Examples of these carboxylic acids are commercial grades of stearic acid and palmitic acid, and mixtures thereof which may contain small amounts of other acids.
- (iv) Esters of polyhydric alcohols such as sorbitan esters or glycerol stearate. Sorbitan esters are the condensation products of sorbitol or iso-sorbitol with fatty acids such as stearic acid. Preferred sorbitan esters are monoalkyl. A common example of sorbitan ester is SPAN 60 (ICI) which is a mixture of sorbitan and isosorbide stearates.
- (v) Fatty alcohols, ethoxylated fatty alcohols, alkyphenols, ethoxylated alkyphenols, ethoxylated fatty amines, ethoxylated monoglycerides and ethoxylated diglycerides.
- (vi) Mineral oils, and polyols such as polyethylene glycol.

These softeners are more definitively described in U.S. Patent 4,134,838 the disclosure of which is incorporated by reference herein. Preferred fabric softeners for use herein are acyclic quaternary ammonium salts. Di(hydrogenated)tallowdimethyl ammonium methylsulfate is most widely used for dryer articles of this invention. Mixtures of the above mentioned tabric softeners may also be used.

The fabric softening composition employed in the present invention contains about 0.1% to about 95% of the fabric softening component. Preferably from about 2% to about 70% and most preferably from about 2% to about 30% of the fabric softening component is employed herein to obtain optimum softening at minimum cost. When the fabric softening component includes a quaternary ammonium salts, the salt is used in the amount of about 2% to about 70%, preferably about 2% to about 30%.

The liquid rinse conditioner composition may also comprise additives which are customary for standard commercial liquid rinse conditioners, for example alcohols, such as ethanol, n-propanol, i-propanol, polyhydric alcohols, for example glycerol and propylene glycol; amphoteric and nonionic surfactants, for example carboxyl derivatives of imidazole,

oxyethylated fatty alcohols, hydrogenated and ethoxylated castor oil, alkyl polyglycosides, for example decyl polyglucose and dodecylpolyglucose, fatty alcohols, fatty acid esters, fatty acids, ethoxylated fatty acid glycerides or fatty acid partial glycerides; also inorganic or organic salts, for example water-soluble potassium, sodium or magnesium salts, non-aqueous solvents, pH buffers, perfumes, dyes, hydrotropic agents, antifoams, anti redeposition agents, polymeric or other thickeners, enzymes, optical brighteners, antishrink agents, stain removers, germicides, fungicides, antioxidants and corrosion inhibitors.

Another aspect of the invention is a tumble dryer sheet article. The conditioning composition of the present invention may be coated onto a flexible substrate which carries a fabric conditioning amount of the composition and is capable of releasing the composition at dryer operating temperatures. The conditioning composition in turn has a preferred melting (or softening) point of about 25°C to about 150°C.

The fabric conditioning composition which may be employed in the invention is coated onto a dispensing means which effectively releases the fabric conditioning composition in a tumble dryer. Such dispensing means can be designed for single usage or for multiple uses. One such multi-use article comprises a sponge material releasably enclosing enough of the conditioning composition to effectively impart fabric softness during several drying cycles. This multi-use article can be made by filling a porous sponge with the composition. In use, the composition melts and leaches out through the pores of the sponge to soften and condition fabrics. Such a filled sponge can be used to treat several loads of fabrics in conventional dryers, and has the advantage that it can remain in the dryer after use and is not likely to be misplaced or lost.

Another article comprises a cloth or paper bag releasably enclosing the composition and sealed with a hardened plug of the mixture. The action and heat of the dryer opens the bag and releases the composition to perform its softening.

A highly preferred article comprises the inventive compositions releasably affixed to a flexible substrate such as a sheet of paper or woven or non-woven cloth substrate. When such an article is placed in an automatic laundry dryer, the heat, moisture, distribution forces and tumbling action of the dryer removes the composition from the substrate and deposits it on the fabrics.

The sheet conformation has several advantages. For example, effective amounts of the compositions for use in conventional dryers can be easily absorbed onto and into the sheet substrate by a simple dipping or padding process. Thus, the end user need not measure the amount of the composition necessary to obtain fabric softness and other benefits.

Additionally, the flat configuration of the sheet-provides a large surface area which results in efficient release and distribution of the materials onto fabrics by the tumbling action of the dryer.

The substrates used in the articles can have a dense, or more preferably, open or porous structure. Examples of suitable materials which can be used as substrates herein include paper, woven cloth, and non-woven cloth. The term "cloth" herein means a woven or non-woven substrate for the articles of manufacture, as distinguished from the term "fabric" which encompasses the clothing fabrics being dried in an automatic dryer.

It is known that most substances are able-to absorb a liquid substance to some degree; however, the term "absorbent", as used herein, is intended to mean a substrate with an absorbent capacity (i.e., a parameter representing a substrates ability to take up and retain a liquid) from 4 to 12, preferably 5 to 7 times its weight of water.

If the substrate is a foamed plastics material, the absorbent capacity is preferably in the range of 15 to 22, but some special foams can have an absorbent capacity in the range from 4 to 12.

Determination of absorbent capacity values is made by using the capacity testing procedures described in U.S. Federal Specifications (UU-T-595b), modified as follows:

- 1. tap water is used instead of distilled water;
- 2. the specimen is immersed for 30 seconds instead of 3 minutes;
- 3. draining time is 15 seconds instead of 1 minute; and
- 4. the specimen is immediately weighed on a torsion balance having a pan with turned-up edges.

Absorbent capacity values are then calculated in accordance with the formula given in said Specification. Based on this test, one-ply, dense bleached paper (e.g., Kraft or bond having

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a basis weight of about 32 pounds per 3,000 square feet) has an absorbent capacity of 3.5 to 4; commercially available household one-ply towel paper has a value of 5 to 6; and commercially available two-ply household towelling paper has a value of 7 to about 9.5.

Suitable materials which can be used as a substrate in the invention herein include, among others, sponges, paper, and woven and non-woven cloth, all having the necessary absorbency requirements defined above.

The preferred non-woven cloth substrates can generally be defined as adhesively bonded fibrous or filamentous products having a web or carded fiber structure (where the fiber strength is suitable to allow carding), or comprising fibrous mats in which the fibers or filaments are distributed haphazardly or in random array (i.e. an array of fibers is a carded web wherein partial orientation of the fibers is frequently present, as well as a completely haphazard distributional orientation), or substantially aligned. The fibers or filaments can be natural (e.g. wool, silk, jute, hemp, cotton, linen, sisal, or ramie) or synthetic (e.g. rayon, cellulose ester, polyvinyl derivatives, polyotefins, polyamides, or polyesters).

The preferred-absorbent properties are particularly easy to obtain with non-woven cloths and are provided merely by building up the thickness of the cloth, i.e., by superimposing a plurality of carded webs or mats to a thickness adequate to obtain the necessary absorbent properties, or by allowing a sufficient thickness of the fibers to deposit on the screen. Any diameter or denier of the fiber (generally up to about 10 denier) can be used, inasmuch as it is the free space between each fiber that makes the thickness of the cloth directly related to the absorbent capacity of the cloth, and which, further, makes the non-woven cloth especially suitable for impregnation with a composition by means of intersectional or capillary action. Thus, any thickness necessary to obtain the required absorbent capacity can be used.

When the substrate for the composition is a non-woven cloth made from fibers deposited haphazardly or in random array on the screen, the articles exhibit excellent strength in all directions and are not prone to tear or separate when used in the automatic clothes dryer.

Preferably, the non-woven cloth is water-laid or air-laid and is made from cellulosic fibers, particularly from regenerated cellulose or rayon. Such non-woven cloth can be lubricated

with any standard textile lubricant.

Preferably, the fibers are from 5mm to 50mm in length and are from 1.5 to 5 denier. Preferably, the fibers are at least partially orientated haphazardly, and are adhesively bonded together with a hydrophobic or substantially hydrophobic binder-resin. Preferably, the cloth comprises about 70% fiber and 30% binder resin polymer by weight and has a basis weight of from about 18 to 45g per square meter.

In applying the fabric conditioning composition to the absorbent substrate, the amount impregnated into and/or coated onto the absorbent substrate is conveniently in the weight ratio range of from about 10:1 to 0.5:1 based on the ratio of total conditioning composition to dry, untreated substrate (fiber plus binder). Preferably, the amount of the conditioning composition ranges from about 5:1 to about 1:1, most preferably from about 3:1 to 1:1, by weight of the dry untreated substrate.

According to one preferred embodiment of the invention, the dryer sheet substrate is coated by being passed over a rotogravure applicator roll. In its passage over this roll, the sheet is coated with a thin, uniform layer of molten fabric softening composition contained in a rectangular pan at a level of about 15g per square yard. Passage for the substrate over a cooling roll then solidifies the molten softening composition to a solid. This type of applicator is used to obtain a uniform homogeneous coating across the sheet.

Following application of the liquefied composition, the articles are held at room temperature until the composition substantially solidifies. The resulting dry articles, prepared at the composition substrate ratios set forth above, remain flexible; the sheet articles are suitable for packaging in rolls. The sheet articles can optionally be slitted or punched to provide a non-blocking aspect at any convenient time if desired during the manufacturing process.

The fabric conditioning composition employed in the present invention includes certain fabric softeners which can be used singly or in admixture with each other.

The liquid rinse conditioner composition according to the invention is usually, but not exclusively, prepared by firstly stirring the active substance, i.e. the hydrocarbon based

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fabric softening component, in the molten state into water, then, where required, adding further desired additives and, finally, after cooling, adding the polyorganosiloxane emulsion.

Examples of suitable textile fibre materials which can be treated with the liquid rinse conditioner composition are materials made of silk, wool, polyamide, acrylics or polyurethanes, and, in particular, cellulosic fibre materials of all types. Such fibre materials are, for example, natural cellulose fibres, such as cotton, linen, jute and hemp, and regenerated cellulose. Preference is given to textile fibre materials made of cotton. The novel liquid rinse conditioner compositions are also suitable for hydroxyl-containing fibres which are present in mixed fabrics, for example mixtures of cotton with polyester fibres or polyamide fibres.

A further aspect of the invention is a textile material treated with a liquid rinse conditioner or a tumble dryer sheet comprising any of the aforementioned polyorganosiloxanes, or a mixture thereof.

A better understanding of the present invention and of its many advantages will be had by referring to the-following Examples, given by\_way of illustration.

#### Example 1

The compositions of fabric softeners given in Table 1 are prepared as follows:

75% of the water is heated to 40°C. The molten fabric softener di-(palmcarboxyethyl-)hydroxyethyl-methylammonium-methosulfate (or Rewoquat WE 38 DPG available from Witco) was added to the heated water under stirring and the mixture was stirred for 1 hour at 40°C. Afterwards the aqueous softener solution was cooled down to below 30°C while stirring. When the solution cooled sufficiently the calculated amount of the particular polyorganosiloxane and magnesium chloride were added. Finally the pH was adjusted to 3.2 with hydrochloric acid 0.1 N, then water was added to make the formulation up to 100%.

These fabric rinse conditioner formulations are normally known under the name of "triple strength" or "triple fold" formula.

Table 1) Examples of rinse conditioner formulations (All Ingredients calculated on active material-):

Formula Number :	0	Α	В	С
	(control)			
Fabric softener (%)	15	15	15	15
Magnesium chloride (%)	0.1	0.1	0.1	0.1
Polyorganosiloxane Emulsion	•	10	. <del>-</del>	-
Type I (%)				
Polyorganosiloxane Emulsion	<del>-</del> .	•	10	•
Type II (%)				
Polyorganosiloxane Emuslion	-	•	<b>-</b> .	10
Type III (%)				
water	added up to 100%			
рН	3.2	3.2	3.2	3.2

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Table 2) Types of emulsions of Polyorganosiloxane of formula 1:

Type Number :	1	II	IN	
R3	0	(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	(CH <sub>2</sub> ) <sub>3</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	
R1	НО	НО	CH₃	
Solid content / 120°C (%)	27 - 29	23 - 25	16.5 - 18.5	
Water content (%)	71.3	73.7	80.4	
x:y ratio	-	95	41	
%N (with respect to Silicone)	0.00	0.03	0.09	
x +y	300 to 1500	300 to 1500	150 to 300	

#### Example 2

The rinse conditioners are applied as follows:

Textile swatches were washed in a washing machine, rinsed and dryed. The pilling was evaluated after 1 wash/rinse-cycle. The textile used was:

Cotton/Polyester 66/34, woven, 85 g/m², bleached, with resin finishing:

30 g/l modified dimethyloldihydroxyethylene urea (65% active material) 9 g/l Magnesiumchloride with 6 H₂O padding with a pick-up of approximately 80% drying at about 110 - 120 °C in a oven Curing at 145°C, 4 minutes

This finishing is according to Oekotex Standard 100

Cotton/polyester woven swatches of size 40cm by 40cm were washed together with ballast material (cotton/polyester). The total load of fabric was 1 kg. The washing machine used was

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a MIELE WS 5425 and the washing temperature 40°C. 2 g/l of ECE Colour Fastness Test Detergent 77 (Formulation January 1977, according to ISO 105-CO6) was used and the washing time was 30 minutes. The rinse conditioner was added in the last rinse cycle. Dosage of rinse conditioner was 5.6 g (calculated on dry material) for 1 kg washload. Without any further rinsing the textile swatches were dryed on a washing line at ambient temperature.

The testing and evaluation of pilling was done as described under point 3 (SN 198525, 1990). A number of 1 means a very strong pilling, a number of 5 means no or very slight pilling

The following results (evaluated after 1000 rotations) have been found:

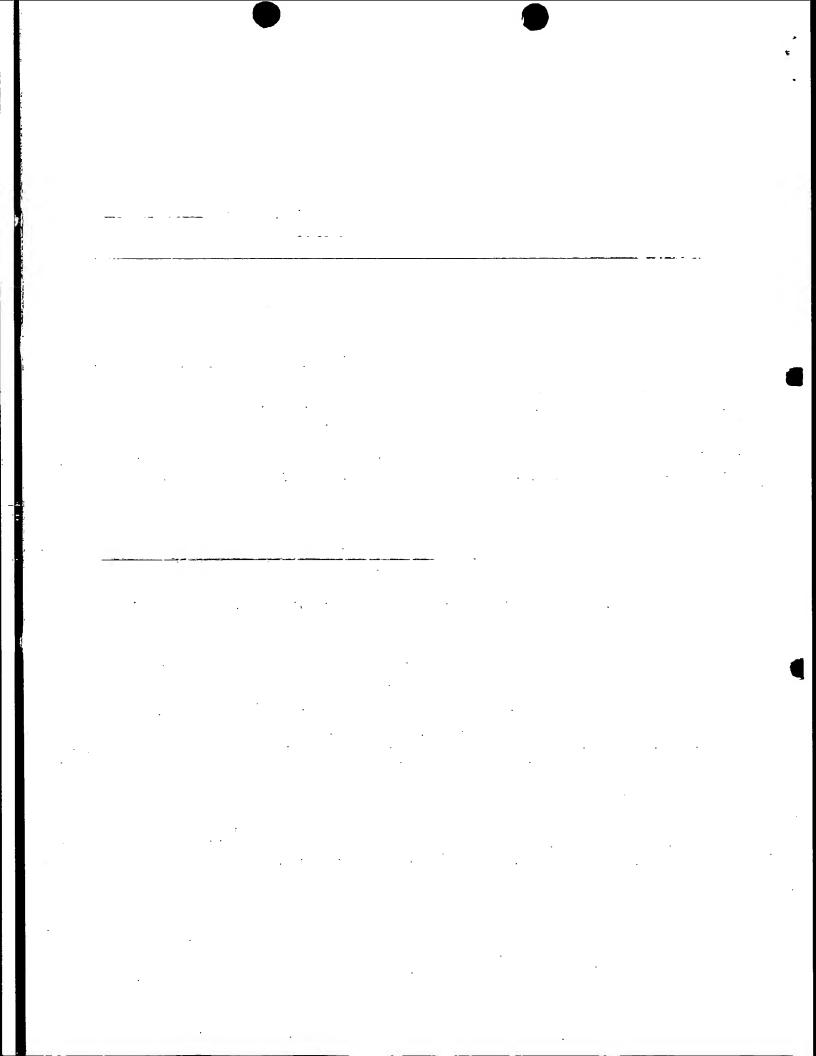
Rinse conditioner sample 0 (control):

1-2

Rinse conditioner sample A:

2-3

These results show a marked improvement in antipilling for the textile fabric material treated —with compositions of the present invention.



#### WHAT IS CLAIMED IS:

1. A method of use of compositions which comprise: dispersed polyorganosiloxanes of formula (1)

(1) 
$$\overrightarrow{R} - Si - O = \begin{cases} CH_3 \\ | \\ Si - O \end{cases} = \begin{cases} CH_3 \\ | \\ Si - O \end{cases} = \begin{cases} CH_3 \\ | \\ Si - O \end{cases} = \begin{cases} CH_3 \\ | \\ Si - O \end{cases} = \begin{cases} CH_3 \\ | \\ CH_3 \end{cases} = CH_3 \\ | \\ CH_3 \end{cases} = \begin{cases} CH_3 \\ | \\ CH_3 \end{cases} = CH_3 \\ | \\ CH_3 \\ | \\ CH_3 \end{cases} = CH_3 \\ | \\ CH_3 \\ | \\ CH_3 \\ | \\ CH_3 \\ | \\$$

wherein

R<sup>1</sup> is OH, OR<sup>2</sup> or CH<sub>3</sub>

R<sup>2</sup> is CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>

R<sup>3</sup> is CH<sub>3</sub>, CH<sub>2</sub>CHR<sup>4</sup>CH<sub>2</sub>NHR<sup>5</sup>, or CH<sub>2</sub>CHR<sup>4</sup>CH<sub>2</sub>N(COCH<sub>3</sub>)R<sup>5</sup>

 $R^4$  is H or CH<sub>3</sub>  $R^5$  is H, CH<sub>2</sub>CH<sub>2</sub>NHR<sup>6</sup>, C(=O)-R<sup>7</sup> or (CH<sub>2</sub>)<sub>Z</sub>-CH<sub>3</sub> z is 0 to 7  $R^6$  is H or C(=O)-R<sup>7</sup>  $R^7$  is CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub> or CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH  $R^8$  is H or CH<sub>3</sub> - 29 -

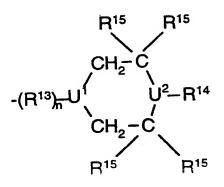
the sum of X and Y is 40 to 1500

or a dispersed polyorganosiloxane which comprises at least one unit of the formula (5);

(5) 
$$(R^9)_V (R^{10})_W \text{ Si-A-B}$$

wherein

 $R^9$  is  $CH_3$ ,  $CH_3CH_2$  or Phenyl  $R^{10}$  is -O-Si or -O- $R^9$  the sum of v and w equals 3, and v does not equal 3  $A = -CH_2CH(R^{11})(CH_2)_K$   $B = -NR^{12}((CH_2)_I-NH)_mR^{12}$ , or



n is 0 or 1 when n is 0,  $U^1$  is N, when n is 1,  $U^1$  is CH l is 2 to 8 k is 0 to 6 m is 0 to 3  $R^{11}$  is H or CH<sub>3</sub>  $R^{12}$  is H, C(=0)- $R^{16}$ , CH<sub>2</sub>(CH<sub>2</sub>)<sub>p</sub>CH<sub>3</sub> or

(6)

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p is 0 to 6

R<sup>13</sup> is NH, O, OCH<sub>2</sub>CH(OH)CH<sub>2</sub>N(Butyl), OOCN(Butyl)

R<sup>14</sup> is H, linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl, Phenyl or CH<sub>2</sub>CH(OH)CH<sub>3</sub>

R<sup>15</sup> is H or linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl

R<sup>16</sup> is CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub> or (CH<sub>2</sub>)<sub>q</sub>OH

q is 1 to 6

U<sup>2</sup> is N or CH

or a dispersed polyorganosiloxane of the formula (8);

(8) 
$$R^{17} - Si - O = CH_3 - CH_3 -$$

wherein

R<sup>3</sup> is as previously defined

 $R^{17}$  is OH,  $OR^{18}$  or  $CH_3$   $R^{18}$  is  $CH_3$  or  $CH_2CH_3$   $R^{19}$  is  $R^{20}$ - $(EO)_m$ - $(PO)_n$ - $R^{21}$ m is 3 to 25 n is 0 to 10  $R^{20}$  is  $CH_2CH(R^{22})(CH_2)_pR^{23}$ p is 1 to 4  $R^{21}$  is H,  $R^{24}$ ,  $CH_2CH(R^{22})NH_2$  or  $CH(R^{22})CH_2NH_2$ 

R<sup>22</sup> is H or CH<sub>3</sub>

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 $R^{23}$  is O or NH  $R^{24}$  is linear or branched  $C_1$ - $C_8$  alkyl or  $Si(R^{25})_3$   $R^{25}$  is  $R^{24}$ , OCH<sub>3</sub> or OCH<sub>2</sub>CH<sub>3</sub> EO is -CH<sub>2</sub>CH<sub>2</sub>O-PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O-the sum of  $X^1, Y^1$  and S is 40 to 1500

or a dispersed polyorganosiloxane of the formula (9);

$$(9) \quad H_{3}C - Si - O = \begin{bmatrix} CH_{3} \\ Si - O \end{bmatrix} = \begin{bmatrix} CH_{3} \\ Si - O$$

R<sup>26</sup> is linear or branched C₁ - C₂₀ alkoxy, CH₂CH(R⁴)R<sup>29</sup>

R4-is-as-previously-defined

R<sup>29</sup> is linear or branched C<sub>1</sub> - C<sub>20</sub> alkyl

 $R^{27}$  is aryl, aryl substituted by linear or branched  $C_1$  -  $C_{10}$  alkyl, linear or branched  $C_1$  -  $C_{20}$  alkyl substituted by aryl or aryl substituted by linear or branched  $C_1$  -  $C_{10}$  alkyl  $R^{28}$  is

the sum of  $X^2$ ,  $X^3$ ,  $X^4$  and  $Y^2$  is 40 to 1500, wherein  $X^3$ ,  $X^4$  and  $Y^2$  may be independently of each other 0;

or a mixture thereof for the antipilling treatment of textile fibre materials.

2. A method according to claim 1 wherein the polyorganosiloxane is of formula (1):

(1) 
$$R^{1} - S_{1} - O = CH_{3}$$
  $CH_{3}$   $CH_{3}$ 

wherein
R<sup>1</sup> is OH, OR<sup>2</sup> or CH<sub>3</sub>
R<sup>2</sup> is CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>
R<sup>3</sup> is CH<sub>3</sub>, CH<sub>2</sub>CHR<sup>4</sup>CH<sub>2</sub>NHR<sup>5</sup>, or

R<sup>4</sup> is H or CH<sub>3</sub>
R<sup>5</sup> is H, CH<sub>2</sub>CH<sub>2</sub>NHR<sup>6</sup>, C(=0)-R<sup>7</sup>
R<sup>6</sup> is H or C(=0)-R<sup>7</sup>
R<sup>7</sup> is CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub> or CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
R<sup>8</sup> is H or CH<sub>3</sub>
the sum of X and Y is 40 to 1500

or a dispersed polyorganosiloxane which comprises at least one unit of the formula (5);

(5) 
$$(R^9)_V (R^{10})_W \text{Si-A-B}$$

wherein

 $R^9$  is  $CH_3$ ,  $CH_3CH_2$   $R^{10}$  is -O-Si or -O- $R^9$ the sum of v and w equals 3, and v does not equal 3  $A = -CH_2CH(R^{11})(CH_2)_K$ B = - 33 -

(6)

n is 1

U1 is CH

k is 0 to 6

R<sup>11</sup> is H or CH<sub>3</sub>

R<sup>13</sup> is OOCN(Butyl)

R<sup>14</sup> is H, linear C<sub>1</sub>-C<sub>4</sub> alkyl, Phenyl

R<sup>15</sup> is H or linear C<sub>1</sub>-C<sub>4</sub> alkyl

U<sup>2</sup> is N

or a dispersed polyorganosiloxane of the formula (8);

(8) 
$$R^{17} - Si - O = CH_3$$
 $CH_3$ 
 $CH_3$ 

wherein

R3 is as previously defined

R<sup>17</sup> is OH, OR<sup>18</sup> or CH<sub>3</sub>

R<sup>18</sup> is CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>

 $R^{19}$  is  $R^{20}$ -(EO)<sub>m</sub>-(PO)<sub>n</sub>- $R^{21}$ 

m is 3 to 25

n is 0 to 10

R<sup>20</sup> is CH<sub>2</sub>CH(R<sup>22</sup>)(CH<sub>2</sub>)<sub>p</sub>R<sup>23</sup>

p is 1 to 4

R<sup>21</sup> is H, R<sup>24</sup>, CH<sub>2</sub>CH(R<sup>22</sup>)NH<sub>2</sub> or CH(R<sup>22</sup>)CH<sub>2</sub>NH<sub>2</sub>

R<sup>22</sup> is H or CH₃

R<sup>23</sup> is O or NH

R<sup>24</sup> is linear or branched C<sub>1</sub>-C<sub>3</sub> alkyl or Si(R<sup>25</sup>)<sub>3</sub>

R<sup>25</sup> is R<sup>24</sup>, OCH<sub>3</sub> or OCH<sub>2</sub>CH<sub>3</sub>

EO is -CH2CH2O-

PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O-

the sum of X<sub>1</sub>,Y<sub>1</sub> and s is 40 to 1500

or a dispersed polyorganosiloxane of the formula (9);

$$(9) \quad H_{3}C = -S_{i} = O = -$$

R<sup>26</sup> is linear C<sub>1</sub> - C<sub>20</sub> alkoxy,

R4 is as previously defined

R<sup>29</sup> is linear C<sub>1</sub> - C<sub>20</sub> alkyl

R<sup>27</sup> is, CH<sub>2</sub>CH(R<sup>4</sup>)Phenyl

R<sup>28</sup> is

the sum of  $X^2$ ,  $X^3$ ,  $X^4$  and  $Y^2$  is 40 to 1500, wherein  $X^3$ ,  $X^4$  and  $Y^2$  may be independently of each other 0;

or a mixture thereof.

3. A method according to claim 1 wherein the polyorganosiloxane is of formula (1):

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(1) 
$$R^{1} - S_{1} - O = CH_{3}$$
  $CH_{3}$   $CH_{3}$ 

wherein R<sup>1</sup> is OH or CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub> or CH<sub>2</sub>CHR<sup>4</sup>CH<sub>2</sub>NHR<sup>5</sup>, R<sup>4</sup> is H or CH<sub>3</sub>, R<sup>5</sup> is CH<sub>2</sub>CH<sub>2</sub>NHR<sup>6</sup>, R<sup>6</sup> is H, and the ratio of X:Y is 25:1 to 220:1 and the sum of X and Y is from 300 to 1500 siloxane units.

4. A method according to claim 1 wherein the polyorganosiloxane is of formula (8):

$$(8) \quad R^{17} - Si - O = \begin{cases} CH_3 \\ Si - O \end{cases} =$$

wherein R<sup>17</sup> is OH or CH<sub>3</sub>, R<sup>3</sup> is CH<sub>3</sub>, CH<sub>2</sub>CHR<sup>4</sup>CH<sub>2</sub>NHR<sup>5</sup>, R<sup>4</sup> is H or CH<sub>3</sub>, R<sup>5</sup> is H, R<sup>19</sup> is R<sup>20</sup>-(EO)<sub>m</sub>-(PO)<sub>n</sub>-R<sup>21</sup> (where m is 3 to 25 and n is 0 to 10), R<sup>20</sup> is CH<sub>2</sub>CH(R<sup>22</sup>)(CH<sub>2</sub>)<sub>p</sub>R<sup>23</sup> (where p is 1 to 4), R<sup>21</sup> is H, R<sup>22</sup> is H or CH<sub>3</sub>, R<sup>23</sup> is O, EO is -CH<sub>2</sub>CH<sub>2</sub>O-, PO is -CH(CH<sub>3</sub>)CH<sub>2</sub>O- or -CH<sub>2</sub>CH(CH<sub>3</sub>)O, the sum of X<sup>1</sup>,Y<sup>1</sup> and S is 150 to 1500 and the ratio of X:S is 25:1 to 220:1.

5. A method according to claim 4 wherein the polyorganosiloxane compositions comprises an additional polyorganosiloxane of the formula (11):

wherein g is

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and G is C<sub>1</sub> to C<sub>20</sub> alkyl.

- 6. A method of use according to any of claims 1 to 5 wherein the composition is used in a liquid rinse conditioner composition.
- 7. A method of use according to any of claims 1 to 6 wherein the composition is used in a tumble dryer sheet composition.
- 8. A method of use according to any of claims 1 to 7 in which the polyorganosiloxane is nonionic or cationic.
- 9. A method of use according to any of claims 1 to 8 in which the polyorganosiloxane aqueous emulsion has a solids content of 5 to 70 % at a temperature of 120°C.
- 10. A method of use according to any of claims 1 to 9 in which the polyorganosiloxane aqueous emulsion contains a water content of 25 to 90 % by weight based on the total weight of the emulsion.
- 11. A method of use according to claims 1 to 10 in which the polyorganosiloxane aqueous emulsion has a pH value from 2.5 to 9.
- 12. A method of use according to claims 1 to 11 in which the nitrogen content of the aqueous emulsion due to the polyorganosiloxane is from 0.001 to 0.25 % with respect to the silicon content.
- 13. A method of use according to any of claims 1 to 12 in which the aqueous composition comprises:

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- a) 2 to 70 % by weight based on the total weight of the composition of polyorganosiloxane, or a mixture thereof; preferably 2 to 35 % by weight based on the total weight of the composition of polyorganosiloxane, or a mixture thereof;
- b) 0.2 to 30 % by weight based on the total weight of the composition of an emulsifier, or a mixture thereof; preferably 0.2 to 10 % by weight based on the total weight the composition of an emulsifier, or a mixture thereof;
- c) 0 to 25 % by weight based on the total weight of the composition of a polyethylene, or a mixture thereof; preferably 0 to 12 % by weight based on the total weight of the composition of a polyethylene, or a mixture thereof;
- d) 0 to 20 % by weight based on the total weight the composition of a fatty acid alkanolamide, or a mixture thereof; preferably 0 to 8 % by weight based on the the composition of total weight of a fatty acid alkanolamide, or a mixture thereof;
- e) 0 to 10 % by weight based on the total weight of the composition of a polysilicic acid; preferably 0 to 5 % by weight based on the total weight of the composition of a polysilicic acid:
- f) water to 100 %.

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- 14. A liquid rinse conditioner composition comprising a polyorganosiloxane as defined in claim 1, or mixtures thereof.
- 15. A tumble dryer sheet composition comprising a polyorganosiloxane as defined in claim 1, or mixtures thereof.
- 16. A textile material treated in a laundry operation with a liquid rinse conditioner comprising a polyorganosiloxane as defined in claim 1, or a mixture thereof.
- 17. A textile material treated with a tumble dryer sheet comprising a polyorganosiloxane as defined in claim 1, or a mixture thereof.

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### **Abstract**

The present invention relates to the use of selected polyorganosiloxanes, or mixtures thereof, liquid rinse conditioner compositions or tumble dryer sheet compositions and to the rinse-added and tumble dryer sheet compositions themselves, in particular it relates to textile softening compositions for use in a textile laundering operation to provide liquid rinse conditioners or tumble dryer sheets which impart excellent antipilling benefits on the textile.

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